Project Report: Evolution of atmospheric O_2, climate, and biosphere – Ohmoto

Project Investigator: ***Hiroshi Ohmoto***

Project Progress

The mass–independent fraction of sulfur isotopes, possibly due to SO_2 photolysis in the atmosphere of early Earth, is of significant scientific interest. Preliminary undertakings were done in our lab employing a pump–probe femtosecond laser technique, coupled with time–of–flight mass spectrometry, to the study of SO_2 photolysis. The results will eventually shed light on unanswered questions regarding the role atmospheric conditions had on the sulfur isotope fractionation in early Earth.

In an experiment performed in our lab, the S–O bond cleavage resulting from dissociation along the ¼ state surface, is found to occur in only 195 fs for the $^{34}SO^{2+}$ species relative to 230 fs for the $^{32}SO^{2+}$ transient. Similarly, the $^{34}SO^{+}$ photolysis product exhibits a growth of approximately 195 fs as compared to a growth of 225 fs, which is observed for the $^{32}SO^{+}$ product. The results indicate a kinetic isotope effect is operative when comparing the excited dynamics of the $^{32}SO_2$ and $^{34}SO_2$ isotopic species. Considering SO_2, where we let k_{32} and k_{34} represent the decay rates of the $^{32}SO_2$ and $^{34}SO_2$ molecules, respectively, k_{32} = 4.34 ps–1 (230 fs) and k_{34} = 5.12 ps–1 (195 fs). The ratio k_{32}/k_{34} = 0.848, indicating a small inverse kinetic isotope effect. This effect was found to be reproducible. Kinetic isotope effects have been observed in a few pump–probe experiments. While a complete review is not appropriate here, it is worthwhile to mention the report of Radloff and co–workers regarding the dissociation of CS_2. It was determined that $C^{32}S^{34}S$ dissociated in 170 fs as compared to $C^{32}S_2$ which dissociated in 210 fs, also indicating a surprising and unexpected inverse kinetic isotope effect similar to that measured and reported by us.

The development of the techniques and the construction of the equipment necessary to perform further high resolution pump–probe and mass spectrometry experiments are underway. We are currently constructing a new detection system using state–of–the–art–equipment to achieve the highest possible mass and intensity resolution with our time–of–flight mass spectrometer. We have purchased a high–sensitivity detection system that will enable the detection of low–abundance isotopes. The high voltage connections needed to transfer the necessary 10,000 V to the detector have been installed in our mass spectrometer along with the high voltage power supply and

associated cables. In addition, mounting hardware for the detector itself is being fabricated. Also, the performance of a broad bandwidth high−speed 8−bit oscilloscope and a lower bandwidth but higher resolution 12−bit digitizer is being evaluated to determine how these devices can be used to quire the ion signal with the highest possible resolution. Also, methods are being developed to calibrate the instrument for the accurate determinations of isotope ratios by using species of known isotopic abundance with a range of masses and isotopic ratios. Improvements and modifications are also being made to the laser system to be used for photoexcitation and photoionization of SO_2 in order to access the electronic excited states relevant to the sulfur isotope fractioning process.